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Role of Biopolymers in Green Nanotechnology

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1. Introduction

1.1 Green nanotechnology

There is currently considerable interest in processing polymeric composite materials filled with nanosized rigid particles. This class of material called “nanocomposites” describes two-phase materials where one of the phases has at least one dimension lower than 100 nm [13]. Because the building blocks of nanocomposites are of nanoscale, they have an enormous interface area. Due to this there are a lot of interfaces between two intermixed phases compared to usual microcomposites. In addition to this, the mean distance between the particles is also smaller due to their small size which favors filler-filler interactions [14]. Nanomaterials not only include metallic, bimetallic and metal oxide but also polymeric nanoparticles as well as advanced materials like carbon nanotubes and dendrimers, However considering environmental hazards, research has been focused on various means which form the basis of green nanotechnology.

1.2 Dual role of biopolymers

Various biopolymers such as starch and cellulose have been of increased interest due to more environmentally aware consumers, increased price of crude oil and global warming. Due to various advantages like renewability, non-toxicity and biocompatibility, their **biocomposites** are used in variety of applications, like therapeutic aids, medicines, coatings, food products and packing materials. **Biocomposites** are composite materials comprising one or more phase(s) derived from a biological origin. In terms of the reinforcement, this could include plant fibers such as cotton, flax, hemp or fibers from recycled wood or waste paper, or even by-products from food crops. The manufacturing of true biocomposites demands that the matrix be made predominantly from renewable resources, although the current state of biopolymer technology dictates that synthetic thermoplastics and thermosets dominate commercial biocomposite production.

This chapter describes two important and diverse roles played by polysaccharides in development of biocomposites viz. **as reinforcing agents in polymers matrix and second as matrix for synthesis of green metal nanocomposites**

1.3 Polysaccharides as reinforcing agents in bionanocomposites

The variety of nanofillers for development of nanocomposites is restricted due to various reasons such as

- limited availability
- cost and
- tendency to aggregate which may prevents high level of dispersion

Hence polysaccharides have been viewed as a potential renewable source of nanosized reinforcement. Being naturally found in a semicrystalline state, aqueous acids can be employed to hydrolyze the amorphous sections of the polymer. As a result the crystalline sections of these polysaccharides are released, resulting in individual monocrystalline nanoparticles [13]. The concept of reinforced polymer materials with polysaccharide nanofillers has known rapid advances leading to development of a new class of materials called **Bionanocomposites**, which successfully integrates the two concepts of biocomposites and nanometer sized materials. The first part of the chapter deals with the synthesis of polysaccharide nanoparticles and their performance as reinforcing agents in bionanocomposites.

1.4 Metal-polysaccharide nanocomposites

In the past few decades, many efforts have been made in the synthesis of metal nanoparticles because of their unusual properties and potential applications in optical, electronic, catalytic, and magnetic materials. Conventional methods of their synthesis involves chemical agents like sodium borohydride and hydrazine hydrate. All these chemicals are highly reactive and pose potential environmental and biological risks. Over the past decade, increasing awareness about the environment has led researchers to focus on green synthetic approaches. Utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy. The later part of the chapter describes the vital role of biopolymers as a matrix for the fabrication of metal nanoparticles, eventually leading to synthesis of green metal nanocomposites.

2. Bionanocomposites of natural rubber with polysaccharides

2.1 Composites and fillers

Composites consist of two (or more) distinct constituents or phases, which when combined result in a material with entirely different properties from those of the individual components. Typically, a manmade composite would consist of a reinforcement phase of stiff, strong material, embedded in a continuous matrix phase. This reinforcing phase is generally termed as filler. The matrix holds the fillers together, transfers applied loads to those fillers and protects them from mechanical damage and other environmental factors. The matrix in most common traditional composites comprises either of a thermoplastic or thermoset polymer [1].

The properties of composites are dictated by the intrinsic properties of the constituents. The two most important factors that affect the performance of composites are

- i. **Filler architecture** : Filler geometry to some extent is influenced by the way in which the fillers are extracted and processed. The aspect ratio (the ratio of filler length to diameter) is an important characteristic for any material to be used as filler. Thus fillers with high aspect ratio are long and thin, while those with low aspect ratio are shorter in length and broader in the transverse direction [1].
- ii. **The filler-matrix interface** : The interface between filler and matrix is also crucial in terms of composite performance. The interface serves to transfer externally applied loads to the reinforcement via shear stresses over the interface. Controlling the 'strength' of the interface is very important. Clearly, good bonding is essential if stresses are to be adequately transferred to the reinforcement and hence provide a true reinforcing function [1].

2.2 Polysaccharides as fillers

The concept of reinforced polymer materials with polysaccharides has known rapid advances in the last decade due to following advantages

- renewable nature
- availability
- diversity of the sources
- low density
- low energy consumption
- low cost
- high mechanical properties
- comparatively easy processability due to their nonabrasive nature, which allows high filling levels, resulting in significant cost savings
- relatively reactive surface, which can be used for grafting specific groups.

Owing to the above reasons, some biopolymers have been used directly or after modification, to replace the conventional fillers leading to partial biodegradation. A number of studies have been carried out with an aim to maximize the proportion of renewable resources used while retaining acceptable material properties.

For instance, natural rubber (NR) which is freely and naturally available at low expenses is widely used in industries. The unique mechanical properties of NR result from its highly stereoregular microstructure, the rotational freedom of the α -methylene C-C bonds and from the entanglements resulting from the high molecular weight which contributes to its high elasticity. The properties of NR can be tailored by the addition of fillers of varying surface chemistry and aggregate size/aspect ratio to suit the application concerned.

Carbon black (CB) manufactured by burning oil or natural gas in controlled conditions is the most important reinforcing agent [2]. But because of its origin from petroleum, it causes pollution and gives black color to the rubber. Hence research was focused on the development of other reinforcing agents to replace carbon black in rubber compounds. Silica and other types of fillers have a weaker polymer-filler interaction and are extensively used where a high degree of reinforcement is not essential [3,4]. The use of clay minerals such as montmorillonite (MMT) [8] and organoclays [6] have also been used as fillers in natural rubber. However, these inorganic fillers have a much reduced affinity toward the elastomer components and thus tend to form large aggregates, leading to drawbacks in processing and

poor reinforcement. Hence, besides inorganic sources biomass is increasingly being looked upon as another potential source [7]. A variety of fibers like sisal [8], bamboo [9], short coir fibres [10] etc. have been used to prepare biocomposites of NR.

2.3 Biocomposites of natural rubber with polysaccharide fillers

Polysaccharides such as starch and cellulose have been used as reinforcing agents in natural rubber. Both solution blending and dry mixing methods have been employed for the development of biocomposites and the performance compared with the composites obtained using carbon black. Dry mixing method is more economically viable and environment friendly.

The results of mechanical properties (presented later in this section) showed that up to 20 phr, the biofillers showed superior strength and elongation behavior than CB, cellulose being the best. After 30 phr the mechanical properties of biocomposites deteriorated because of the poor compatibility of hydrophilic biopolymers with hydrophobic natural rubber(results not shown) . While increasing quantity of CB in composites leads to constant increase in the mechanical properties. Scanning electron micrographs revealed presence of polymer-filler adhesion in case of biocomposites at 20 phr.

Thermal stability is a crucial factor when polysaccharides are used as reinforcing agents because they suffer from inferior thermal properties compared to inorganic fillers. However, thermogravimetric analysis (TGA) of biocomposites suggested that the degradation temperatures of biocomposites are in close proximity with those of carbon black composites (Table-1).

Fillers	Degradation temperature (°C) for % wt. loss			Tg °C
	1	10	50	
Starch	128	303	351	-63.14
Cellulose	137	288	325	-62.96
Carbon black	114	304	364	-62.24

Table 1. Thermogravimetry data and Tg values of NR composites containing various fillers

Another major drawback of polysaccharides is their hydrophilic nature leading to low degrees of adhesion between fiber and matrix [11]. Moisture absorption takes place by three types of mechanisms namely diffusion, capillarity, and transport via micro cracks [2]. Among the three, diffusion is considered to be the major mechanism. Water absorption largely depends on the water-soluble or hygroscopic components embedded in the matrix, which acts as a semipermeable membrane. While, fiber/matrix adhesion and fiber architecture also affect the moisture absorption. The results of the water sorption experiment showed an interesting trend. The extent of water uptake was not very significant and also did not increase linearly with amount of filler (Table-2).

The unusual thermal stability and water uptake properties are due to the formation of a three-dimensional network in polysaccharides at high processing temperatures [12].

Owing to the general incompatibility between natural fillers and most polymers, methods of promoting adhesion are frequently needed. Several approaches have been explored, including chemical modification of the filler prior to composite manufacture and introducing compatibilizing agents to the polymer/filler during processing.

Fillers	mole % uptake		
	10 phr	20 phr	30 phr
Starch	1.2359	1.0382	1.0429
Cellulose	1.2065	1.055	1.0324
Carbon black	1.1938	1.0272	1.0108

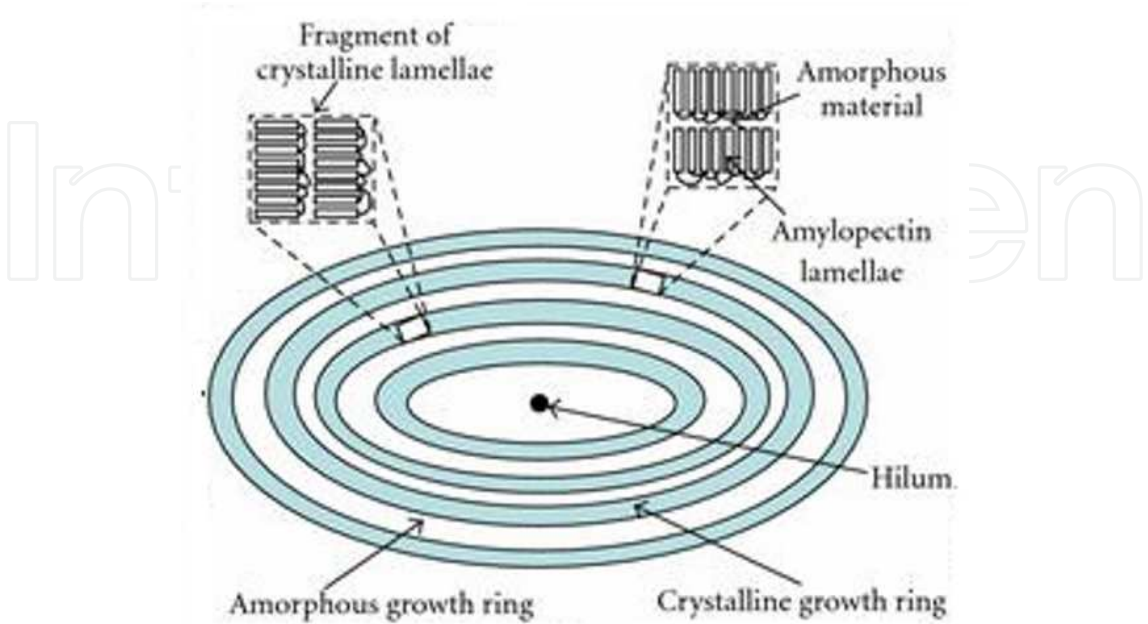
Table 2. Water sorption of NR composites containing various fillers

The main hurdle for the use of starch as a reinforcing phase is its hydrophilicity leading to incompatibility with polymer matrix and poor dispersion causing phase separation. Two strategies have been adopted to improve the performance of polysaccharides.

1. Reduction in particle size of the biopolymers to obtain nanofillers which can result in more uniform distribution within the polymer matrix.
2. Organic modification of the nanofillers to obtain hydrophobic derivatives having improved compatibility with the polymer.

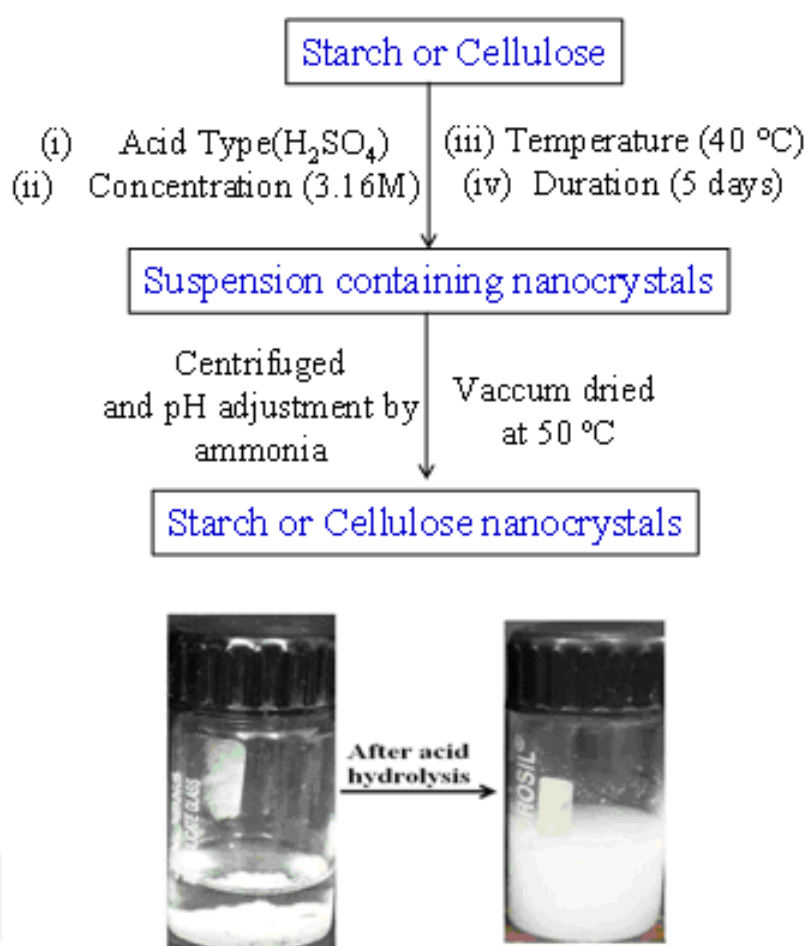
2.4 Polysaccharide nanoparticles and their organic modification

Native starch granules contain more or less concentric “growth rings” that are readily visible by optical or electronic microscopy as seen in Scheme-1 [15]. Acid treatment is needed to reveal the concentric lamellar structure of starch granules. The purpose of this treatment is to dissolve away regions of low lateral order so that the water-insoluble, highly crystalline residue may be converted into a stable suspension by subsequent vigorous mechanical shearing action. Dufresne et. al [16] obtained starch nanocrystals (SN) from waxy corn starch granules as per the conditions optimized as shown in Scheme-2. The insoluble hydrolyzed residue obtained from waxy corn was reported to be composed of crystalline nanoplatelets around 5-7 nm thick with a length of 20-40 nm and a width of 15-30 nm [16].



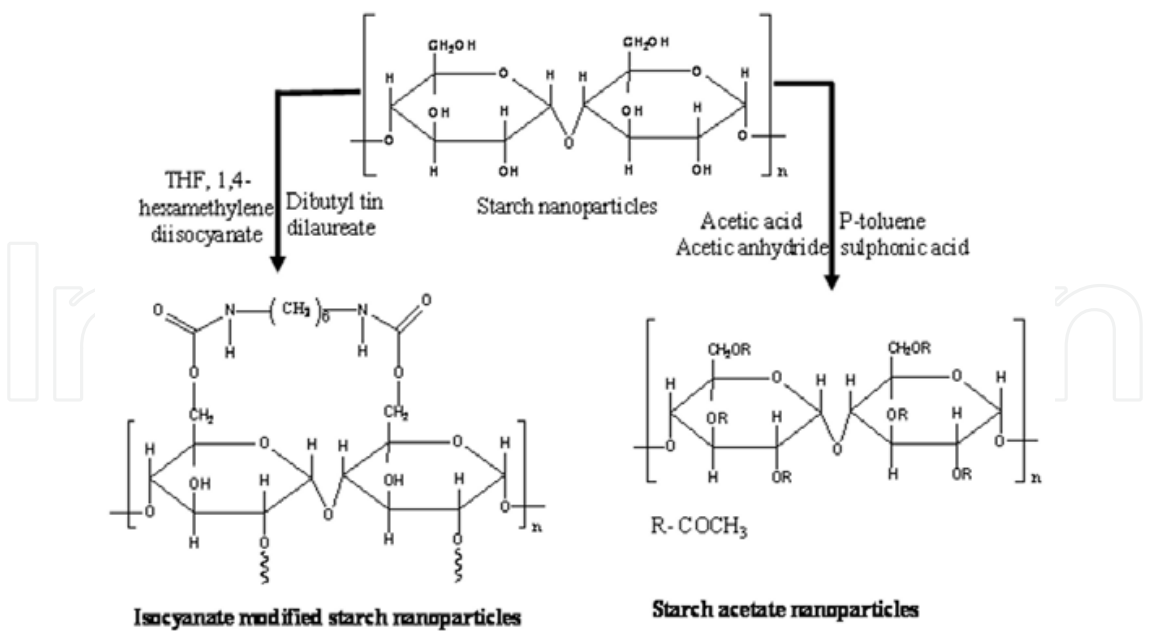
Scheme 1. Structure of starch granule

A similar procedure was adopted for synthesis of nanoparticles of cellulose (CelNPs). The polysaccharide nanoparticles were derivatised under ambient conditions to obtain nanosized hydrophobic derivatives. The challenge here is to maintain the nanosize even after derivatisation due to which less vigorous conditions are preferred. A schematic synthesis of acetyl and isocyanate modified derivatives of starch nanoparticles (SNPs) is shown in scheme 3. The organic modification was confirmed from X-ray diffraction (XRD) pattern which revealed that A- style crystallinity of starch nanoparticles (SNPs) was destroyed and new peaks emerged on derivatisation. FT-IR spectra of acetylated derivatives however showed the presence of peak at 3400 cm^{-1} due to -OH stretching indicating that the substitution is not complete.



Scheme 2. Various conditions and steps involving general synthesis of polysaccharide nanoparticles

In the transmission electron microscopy (TEM) images, the starch nanoplatelets (SNPs) are believed to aggregate as a result of hydrogen bond interactions due to the surface hydroxyl groups [13] (Fig. 1A). Blocking these interactions by relatively large molecular weight molecules obviously improves the individualization of the nanoparticles. The acetylated starch and cellulose nanoparticles (SAcNPs and CelAcNPs) appeared more individualized and monodispersed than their unmodified counterparts with a size of about 50 nm (Fig. 1B & C).



Scheme 3. Organic modification of starch nanoparticles

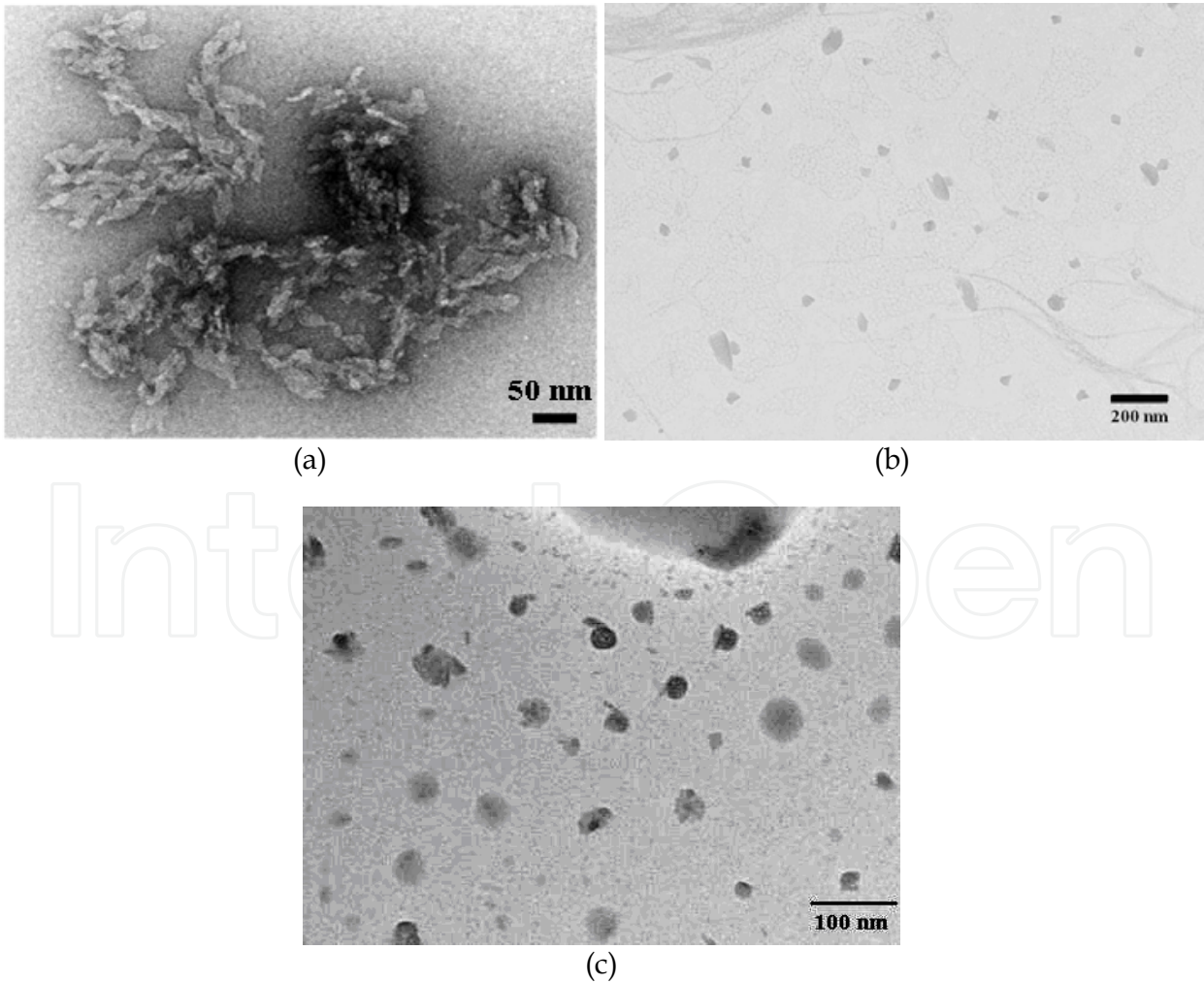
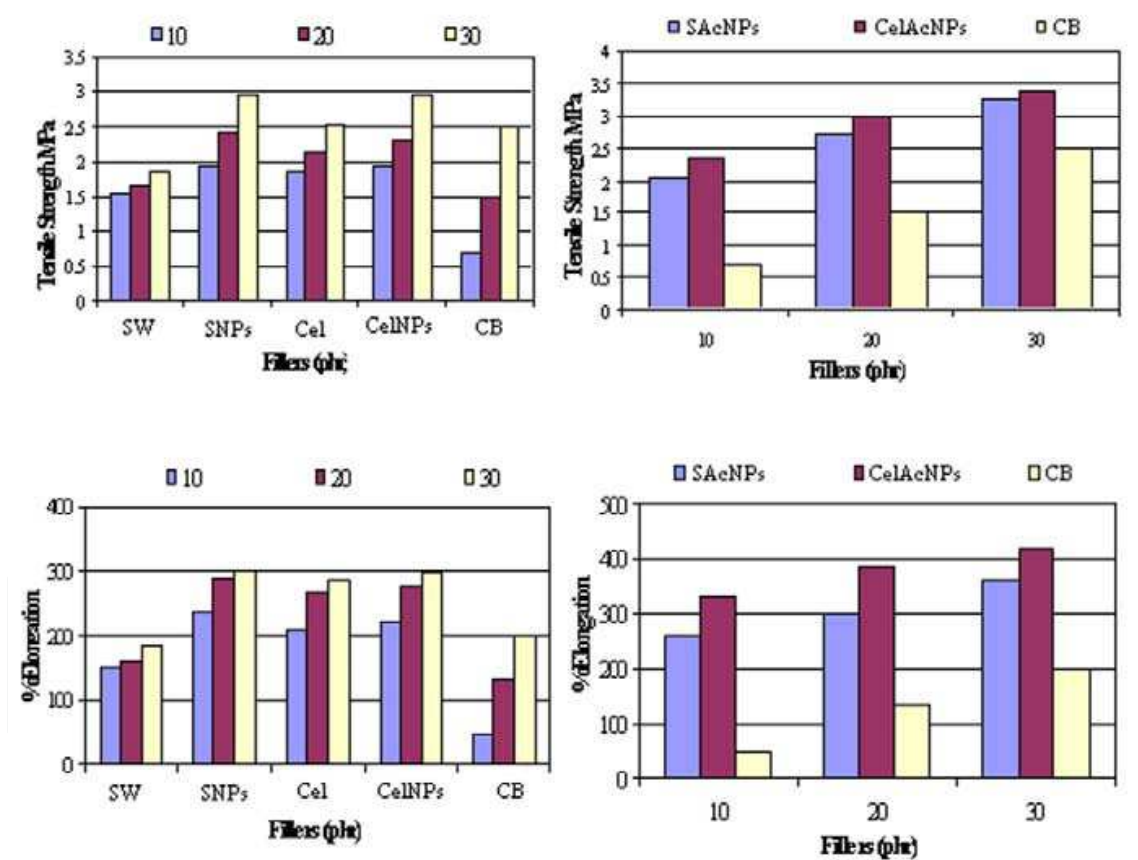


Fig. 1. TEM images of (A) SNPs taken from reference no. 16 (B) SAcNPs and (C) CelAcNPs

2.5 Polysaccharide nanoparticles as reinforcing agents

The unmodified and acetylated nanoparticles were used to develop nanobiocomposites of NR containing 40 phr polysaccharide content and their performance was evaluated. The results obtained from mechanical properties showed that for each measurement, the strain was macroscopically homogenous and uniform along the sample until it breaks. The lack of any necking phenomenon confirms the homogenous nature of these nanocomposites. The stress continuously increases with strain and the amount of fillers. Whereas Angellier et al. [17] observed a decrease in elongation as the amount of filler increases. The initial high stress is due to the reinforcement of the rubber with nanofillers [18]. As the strain increases, stress induced crystallization comes into role, which increases proportionally along with strain. The dispersion of nanofillers leads to an efficient reinforcement, which leads to improved stiffness. The unmodified nanoparticles imparted lower strength due to hydrophilic nature resulting in poor adhesion with NR. As a result the stress transfer from the matrix to the filler is poor and the mechanical properties of nanoparticles are not fully utilized. As the amount of nanofillers increases the tensile strength (T.S.) continued to increase as expected (figure 2). In case of CB composites the initial lower T. S. value rapidly increases from 10 to 30 phr loading but remains



SW- waxy corn starch, SWNPs- starch nanoparticles, Cel- microcrystalline cellulose, CelNPs- cellulose nanoparticles, CB- carbon black, SWAcNPs- waxy starch acetate nanoparticles, CelAcNPs: cellulose acetate nanoparticles.

Fig. 2. Summary of mechanical properties of composites containing various fillers

lower than nanocomposites at all levels. Nanocomposites of acetylated polysaccharide nanoparticles showed not only higher strength but also greater elongation due to the

improved dispersion of filler and better compatibility with NR owing to its hydrophobic nature and small particle size. The behavior is consistent with respect to all the nanofillers. This indicates that the nanofillers used retain the elastic property of natural rubber which is also concluded by dynamic mechanical analysis (discussed later).

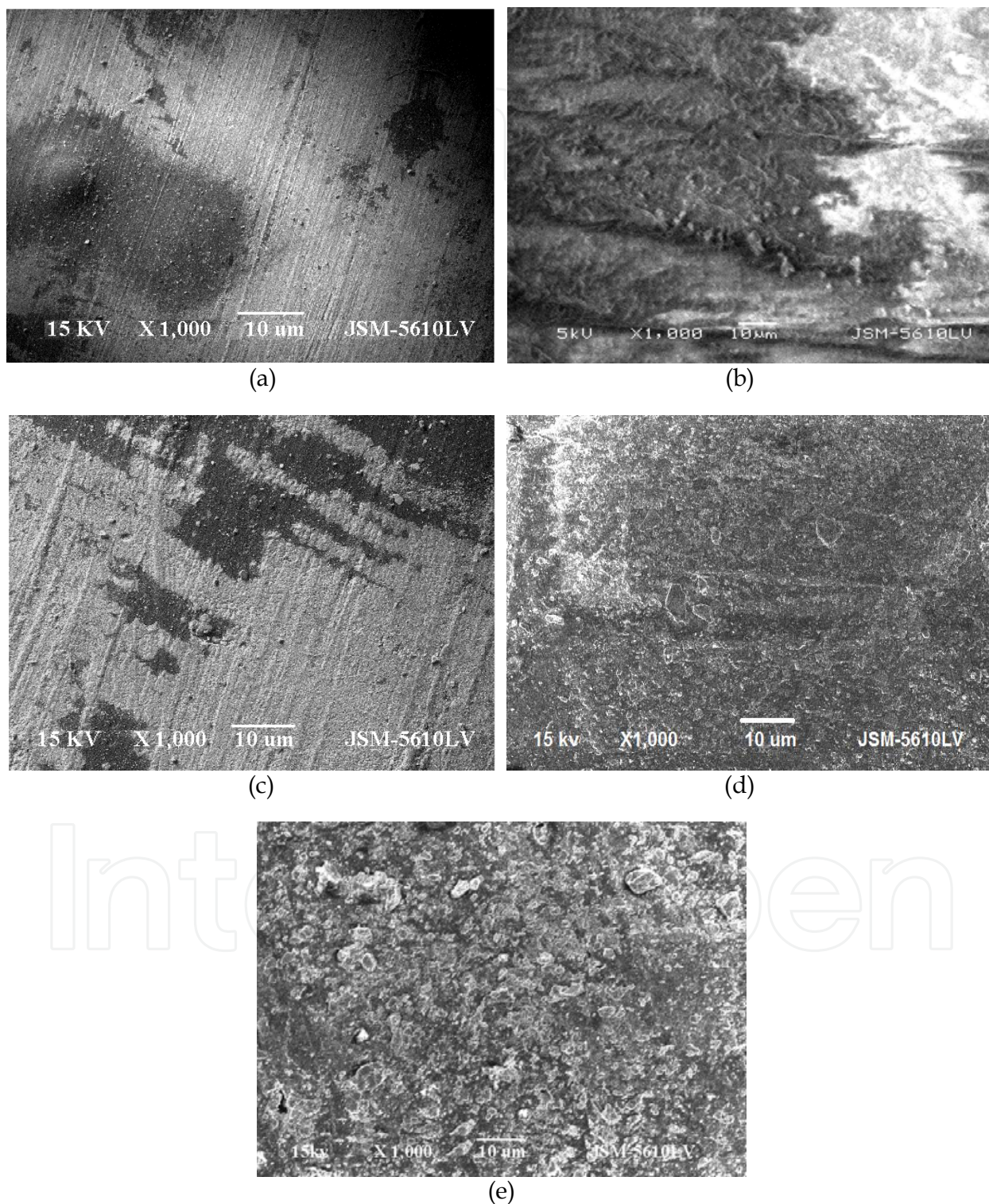


Fig. 3. SE Micrographs of NR composites at 40 phr loading of (A) SAcNPs, (B) CelAcNPs, (C) SNPs, (D) CelINPs and (E) CB

The results of the mechanical properties can be explained on the basis of morphology. The scanning electron micrographs (SEM) of fractured samples of biocomposites at 40 phr loading are shown in figure. 3. It can be seen that all the bionanofillers are well dispersed into polymer matrix without much agglomeration. This is due to the better compatibility between the modified polysaccharides nanoparticles and the NR matrix (Fig. 4A and B). While in case of unmodified polysaccharides nanoparticles the reduction in size compensates for the hydrophilic nature (Fig. 3C and D). In case of CB composites (Fig. 3E) relatively coarse, two-phase morphology is seen.

The $\tan \delta$ curve (Fig. 4) at 1 Hz of nanocomposites showed a broad relaxation process from -80 °C to -10 °C. This may be due to the relaxation of rubber fraction confined inside the layers. The reduction in the $\tan \delta$ maxima suggests a strong adhesion between NR and modified starch nanoparticles. Sliding along the exfoliated interlayer is suppressed [13]. In addition, chain slipping at the outer surfaces of the aggregates is also likely to be hampered. Therefore the loss maximum is smaller in case of the nanocomposite system with the strongest filler matrix coupling.

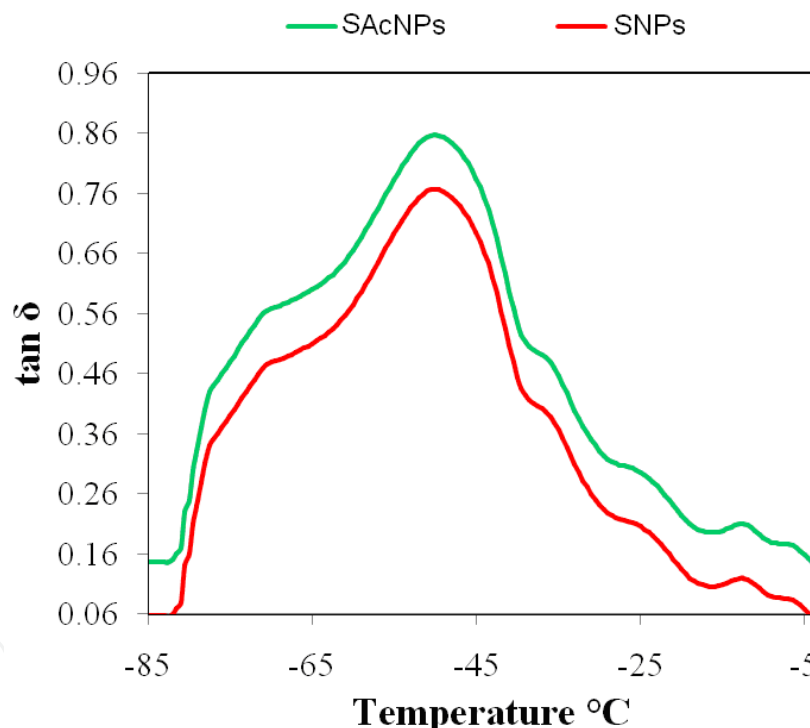


Fig. 4. Effect of nanocomposites on mechanical loss factor $\tan \delta$ vs temperature

Due to the higher performance of cellulosic fillers, highly filled bionanocomposites were developed by incorporation of upto 60 phr (37.5 weight %) cellulosic nanofillers. Cellulose acetate nanoparticles (CelAcNPs) exhibit excellent reinforcing ability upto 50 phr (33.3 weight %) preserving the elastic behavior of nanocomposites (Fig. 5). At still higher loading the performance of carbon black was observed to be much superior to the cellulosic fillers. The results of mechanical properties also indicate that the combined effect of size reduction and organic modification drastically improves the performance of cellulose. Although, a drop in mechanical strength was observed above 50 phr, the cellulosic fillers proved to be potential reinforcing agents even at higher loadings.

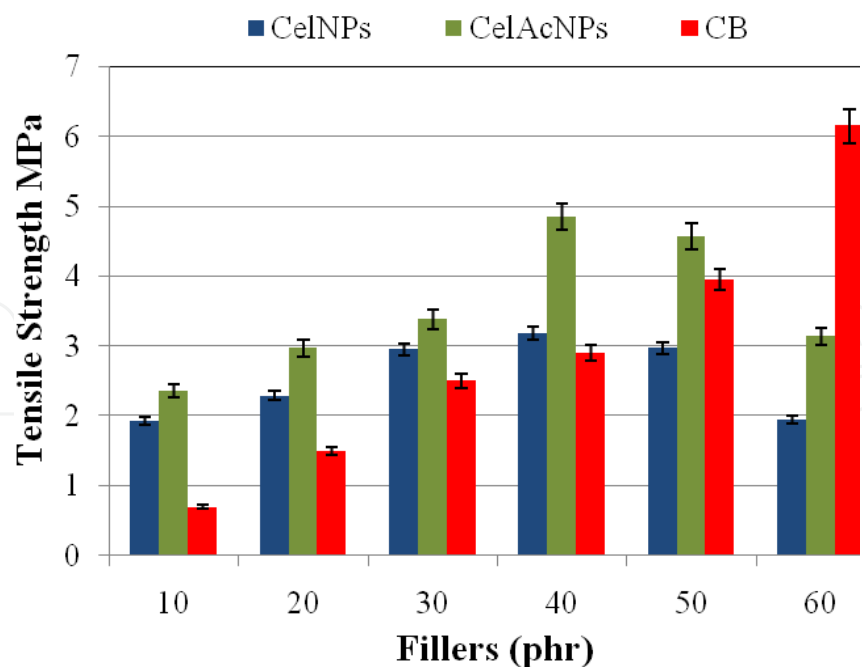


Fig. 5. Tensile strength of highly filled bionanocomposites containing cellulosic fillers

The results of thermal properties support the observation that increased hydrophobicity and reduced particle size of nanofillers imparts rigidity and strength to the network.

Fillers	% mole Uptake					
	Water			Toluene		
	10 phr	30 phr	50 phr	10 phr	30 phr	50 phr
SACNPs	1.13	0.26	0.24	2.76	2.12	1.87
SNPs	3.10	2.44	0.61	1.22	0.34	0.31
CelNPs	1.39	0.79	0.38	2.79	2.36	1.82
CelAcNPs	1.12	0.51	0.21	3.12	2.56	2.02
CB	1.15	0.56	0.31	2.77	1.97	1.42

Table 3. Water and toluene sorption of NR composites containing various fillers

The interaction between polymer matrix and filler leads to the formation of a bound polymer in close proximity to the reinforcing filler, which restricts the solvent uptake [13]. The composites containing acetylated cellulose fillers exhibited higher uptake of toluene compared to water in accordance with their hydrophobic nature.

Overall the results led to the conclusion that acetylated nanoparticles of both starch and cellulose offer potential eco-friendly substitutes for the conventional filler carbon black upto 40 phr. They imparted high mechanical strength and elasticity with minimum compromise in thermal stability and moisture absorption of the resulting bionanocomposites. Cellulose acetate nanoparticles afforded effective reinforcement even upto loadings as high as 50 phr.

3. Metal-polysaccharide nanocomposites

Polymers like polyvinyl pyrrolidone (PVP) [19] and polyacrylamide [20] have been successfully used as the stabilizing agents for synthesis of various metal nanoparticles. Metal polymer nanocomposites exhibit interesting optical and conducting properties [21]. But in the present scenario, increasing awareness about the environment has led researchers to focus on 'green chemistry'. Biopolymers represent suitable matrices for the preparation of metal nanocomposites being generally low cost materials characterized by an easy processing. The inherent biocompatibility and biodegradability of these polymers enable their use in a variety of applications in biotechnology and in environmental protection.

3.1 Starch as a matrix for the synthesis of nanoparticles

Biopolymers like starch and chitosan are reported to have played the role of stabilizers for silver nanoparticles [22]. Starch, for instance, adopts right-handed helical conformation in aqueous solution, in which the extensive number of hydroxyl groups can facilitate the complexation of metal ions to the molecular matrix [23]. The concept of green nanoparticles preparation using starch as stabilizer was first reported by Raveendran et al. [23] where glucose was used as the reducing agent. The synthesis of stable Cu nanoparticles is of particular interest because of its tendency to get oxidised in an aqueous system [24]. Schematic representation of formation of copper nanoparticles in aqueous matrix of biopolymer such as starch can be seen in Fig.6. A typical TEM image of the Cu nanoparticles

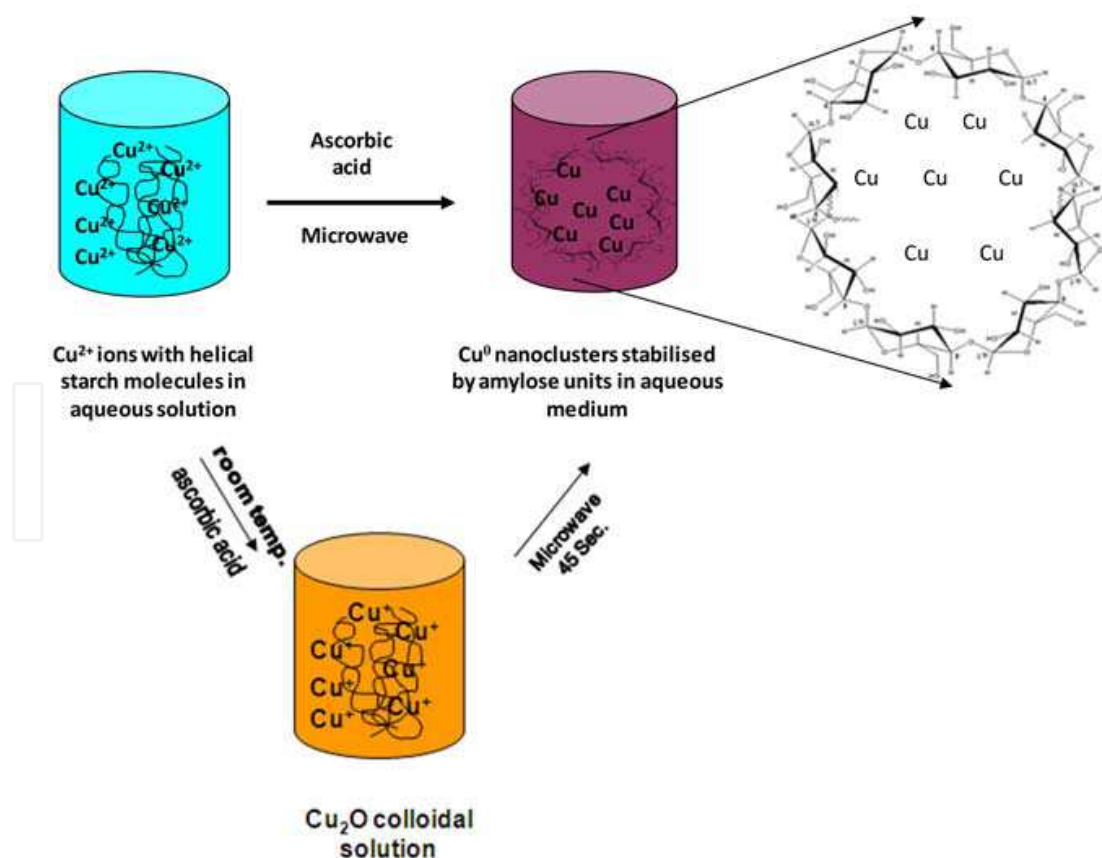


Fig. 6. Schematic representation of synthesis of starch capped copper nanoparticles under microwave conditions

(CuNPs) in Fig. 7 shows the monodisperse and uniformly distributed spherical particles of 10 ± 5 nm diameter. The solution containing nanoparticles of silver was found to be transparent and stable for 6 months with no significant change in the surface plasmon and average particle size. However, in the absence of starch, the nanoparticles formed were observed to be immediately aggregated into black precipitate. The hydroxyl groups of the starch polymer act as passivation contacts for the stabilization of the metallic nanoparticles in the aqueous solution. The method can be extended for synthesis of various other metallic and bimetallic particles as well.

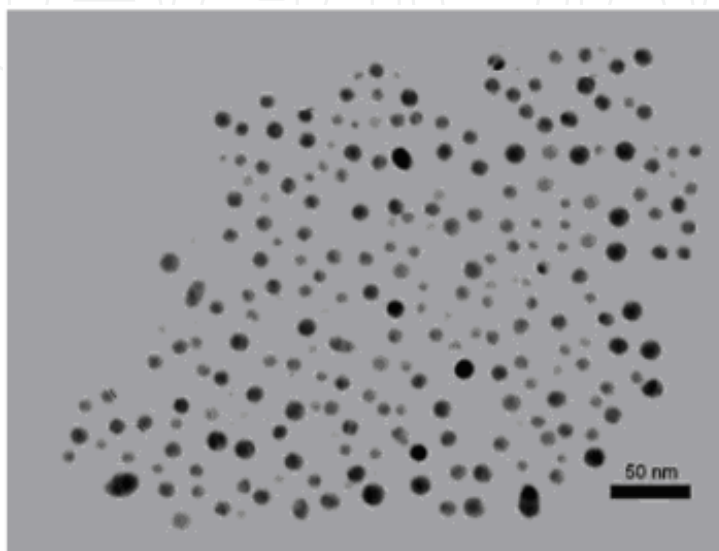


Fig. 7. TEM image of starch capped copper nanoparticles

3.2 Bimetallic nanoparticles

Bimetallic nanoparticles, either as alloys or as core-shell structures, exhibit unique electronic, optical and catalytic properties compared to pure metallic nanoparticles [24]. Cu-Ag alloy nanoparticles were obtained through the simultaneous reduction of copper and silver ions again in aqueous starch matrix. The optical properties of these alloy nanoparticles vary with their composition, which is seen from the digital photographs in Fig. 8. The formation of alloy was confirmed by single SP maxima which varied depending on the composition of the alloy.

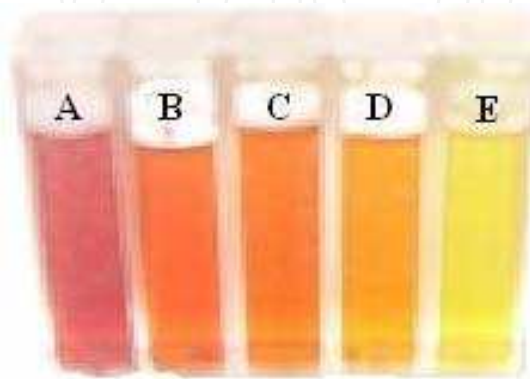


Fig. 8. Digital photograph of starch capped metallic and bimetallic nanoparticles in aqueous medium. A: Cu; B-D: Cu-Ag; E: Ag.

3.3 Biological applications of starch capped nanoparticles

Silver nanoparticles exhibits strong cytotoxicity towards a broad range of microorganisms, and its use as an antibacterial agent is well known [25]. for biological applications. The effective biocidal concentration of silver nanoparticles (AgNPs) is at a nanomolar level in contrast to a micromolar level of silver ions [26]. On the other hand, only a few studies have reported the antibacterial properties of copper nanoparticles. Nevertheless, copper nanoparticles have a significant promise as bactericidal agent [27,28]. The biopolymer matrix offers additional advantages like water solubility and biocompatibility necessary for use in biological applications. Hence, the starch capped water soluble nanoparticles exhibited excellent antibacterial activity against both gram positive and gram negative bacteria at a very low concentration.

The mode of action of starch capped copper nanoparticles (SCuNPs) was compared with that of the well-known antibiotic ampicillin (Fig. 9). There was a drastic decrease in the optical density of compounds containing SCuNPs and ampicillin, ultimately reaching almost zero suggesting that there were no more bacteria present in the culture. Ampicillin at a concentration of 100 $\mu\text{g/ml}$ has the ability to lyse *E.coli* almost immediately [29]. The same effect was produced by SCuNPs at 365 ng/ml concentration. The cell lysis occurs at the expense of the fact that at the point of cell division there occurs a deformation of the cell envelope. The decrease in optical density is possibly associated with the cell-envelope deformation occurring at the point of cell division [30].

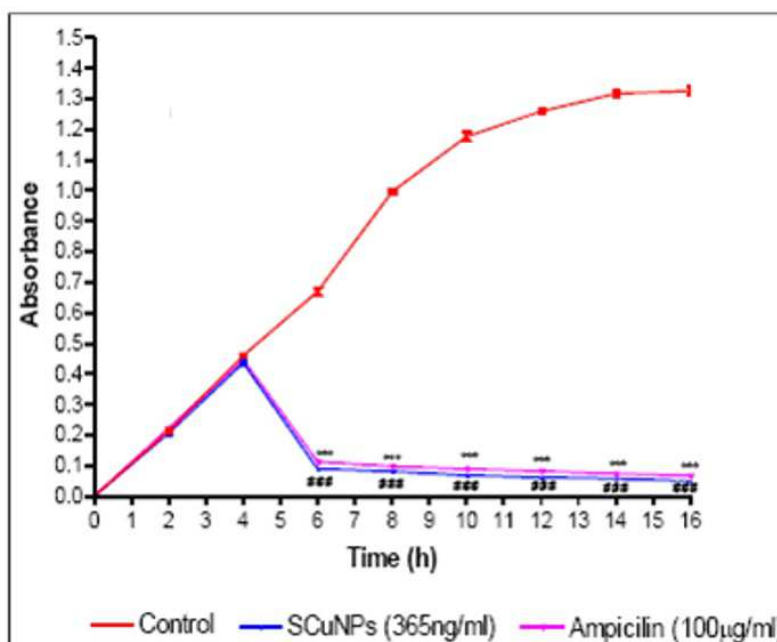


Fig. 9. Comparison of mode of action against *E.coli*: starch capped copper nanoparticles vs. ampicillin

The presence of nanoparticles suspended within the starch matrix would ensure continuous release of ions into the nutrient media. Copper ions released by the nanoparticles may attach to the negatively charged bacterial cell wall and rupture it, thereby leading to protein denaturation and cell death [31]. The attachment of both ions and nanoparticles to the cell wall caused accumulation of envelope protein precursors, which resulted in dissipation of

the proton motive force. Thus it can be concluded that SCuNPs show lytic mode of action against *E.coli* similar to Ampicillin.

The biological impact of starch capped copper nanoparticles on mouse embryonic fibroblast (3T3L1) cells (*in vitro*) was also evaluated by various parameters. More than 85 % of the 3T3L1 cells were found to be viable, even after 20 hours time exposure which implies minimum impact on cell viability and morphology. The study demonstrates dose dependent cytotoxic potential of SCuNPs, that is non cytotoxic in the nanogram dose and moderately cytotoxic in the microgram doses (Fig. 10). Comparison of SCuNPs with Cu^{2+} ions and uncapped copper nanoparticles (UCuNPs) revealed that, ions are more cytotoxic than SCuNPs. This observation supports the theory of slow release of ions from starch coated nanoparticles.

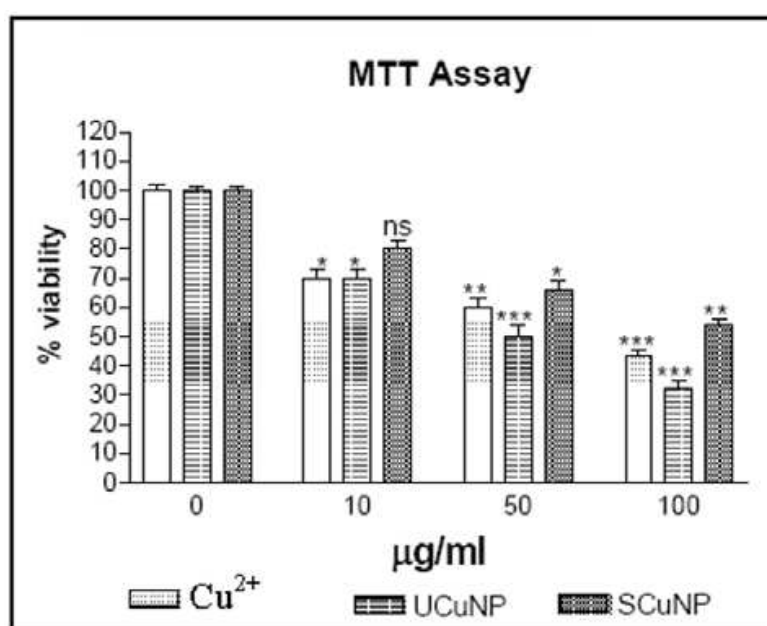


Fig. 10. Effect of starch capped copper nanoparticles on cell viability (MTT assay) in case of mouse embryonic fibroblast (3T3L1).

Visual imaging of cell population (*in vitro*) using low signal-to-noise ratio phase contrast microscopy can enable systematic monitoring measurements of cell quality, development and apoptosis. In the present study, microscopic evaluations as seen in Fig. 11 did not reveal any significant alteration in cellular morphology upto 1000 ng/ml.

Water soluble starch capped nanoparticles proved to be efficient non-cytotoxic bactericidal agents at nanomolar concentrations. The investigation also suggested that starch capped CuNPs have great potential for use in biomedical applications such as cellular imaging or photothermal therapy.

The cytotoxicity potential of the biopolymer capped nanoparticles was evaluated using various parameters like MTT cell viability assay and extracellular lactate dehydrogenase (LDH) release in human lung cancer cells. Other parameters that determine the oxidative stress viz., reactive oxygen species (ROS) generation, intracellular reduced glutathione (GSH), malondialdehyde (MDA), superoxide generation and acridine orange/ethidium bromide staining were also investigated. The study led to the conclusion that copper

nanoparticles were toxic to human lung cancer cells in a dose dependent manner. Further work to use the biopolymer capped copper nanoparticles for targeted in vivo delivery to cancer cells is a challenging task for researchers.

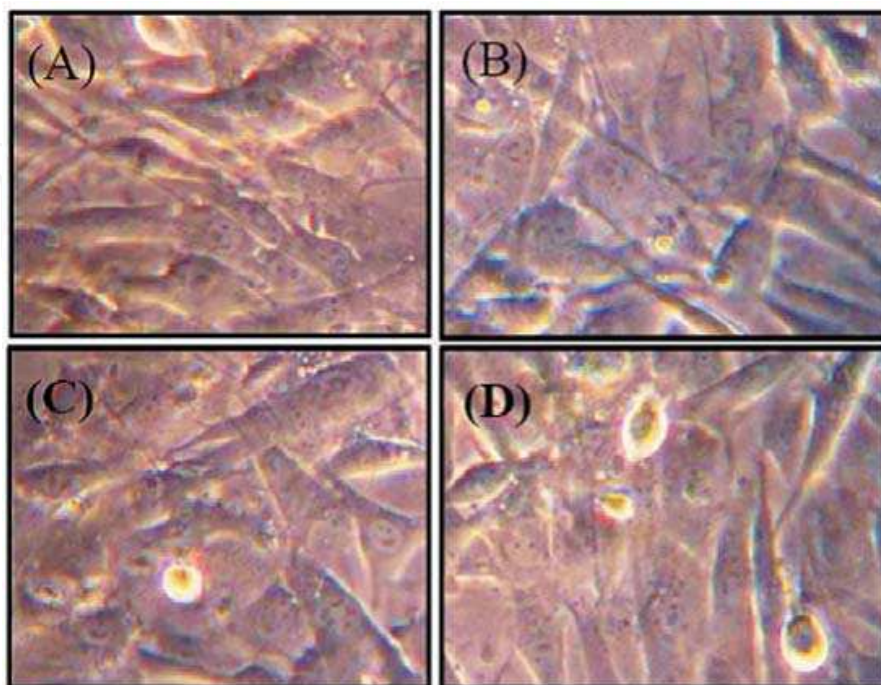


Fig. 11. Photomicrographs of mouse embryonic fibroblast (3T3L1) cells (A) untreated, treated with (B) control (C) 500ng CuNPs, (D) 1000ng CuNPs.

3.4 Starch as morphology directing agent

Silver nanoparticles have been prepared by using disaccharide sucrose and polysaccharides; amylose rich soluble starch and amylopectin-rich waxy corn starch so that the carbohydrates act as both reducing and stabilizing agent. The reduction was fastest in case of sucrose followed by waxy starch and soluble starch; while stability of nanoparticles followed the order soluble starch > waxy corn starch > sucrose [32]. Thus the size and molecular weight were important for stabilization of the nanoparticles. Also in case of starch the reduction occurred only after heating at 80 °C for 4 hrs. This is required because the more hydrolyzed the polysaccharide, the better is its ability to act as reducing agent. As such sucrose cannot act as a reducing agent but in presence of microwave sucrose gets hydrolyzed and the hydrolyzed products then reduce the metal. The time taken for reduction is also very short (30 sec).

The nanoparticles exhibited interesting morphology when synthesized under hydrothermal conditions depending upon the content of amylopectin in carbohydrates. The nanoparticles formed in waxy corn starch matrix were observed to have self-assembled into wire-like structures, (Fig. 12). Although the exact mechanism of the formation of the nanostructures is difficult to know, it was proposed that the chain-shaped structure of starch could serve as a directing template for the growth of silver nanoparticles [32]. Starch is composed of a linear component, amylose and a branched component, amylopectin. The branching is due to 1, 6 acetal linkage in amylopectin which is absent in amylose. It is assumed that as a result of the bond angles in the alpha acetal linkage, amylose forms a spiral structure which helps

in stabilization. While branched polymer might act as a morphology directing agent, facilitating the growth of silver nanowires.

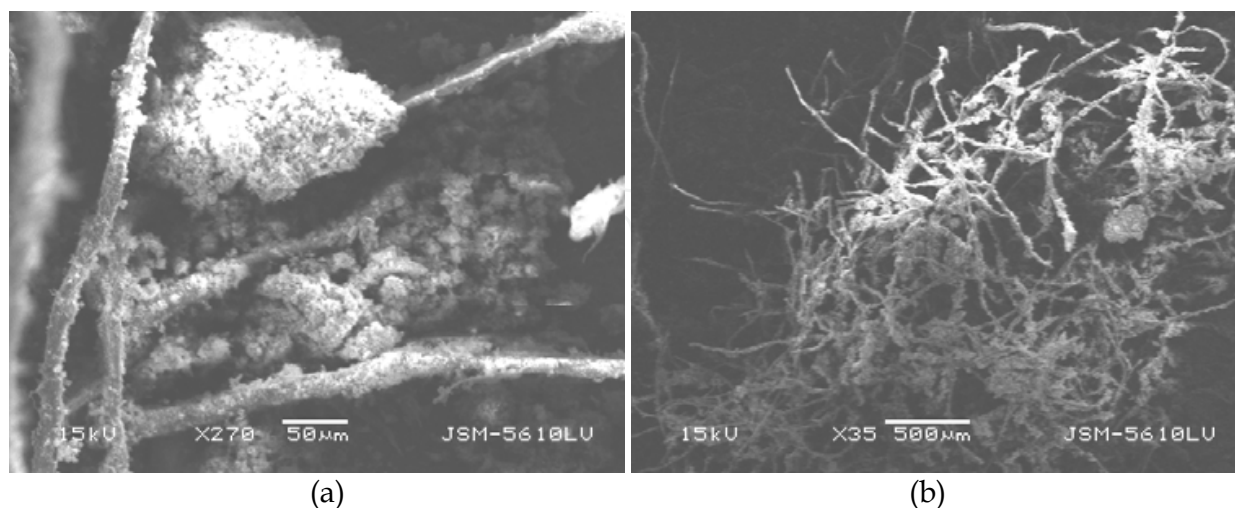


Fig. 12. SEM images of Ag nanostructures in starch matrix (A) 270 x and (B) 35 x

Metal oxide nanostructures, as promising materials, have attracted much attention because of their extraordinary properties in different fields of optics, optoelectronics, catalysts, biosensors and so on. A simple and eco-friendly method was developed for the preparation of well-controlled, uniform Cu_2O dendrites using only starch as stabilizing, reducing as well as morphology directing agent in an aqueous solution by hydrothermal route. The digital photograph in Fig. 13 indicates the colour changes that occur as the reaction proceeds in a sealed pyrex tube. At 180 °C, as the time increased the self assembling of the nanoparticles into distinct continuous dendrites is clearly visible in figure 14A and B. The schematic diagram in figure 14C depicts the growth of three dimensional dendrites over the primary structure [33].

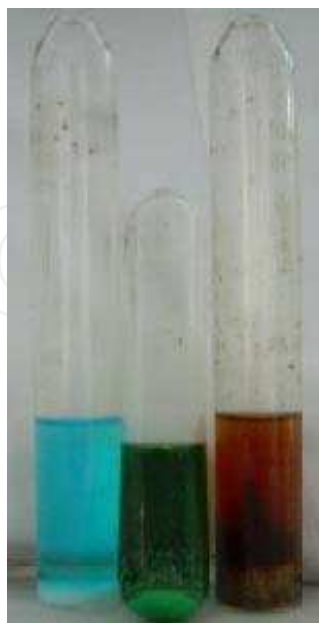


Fig. 13. Digital photograph showing various stages of the hydrothermal reduction of reaction of Cu_2O in a sealed tube.

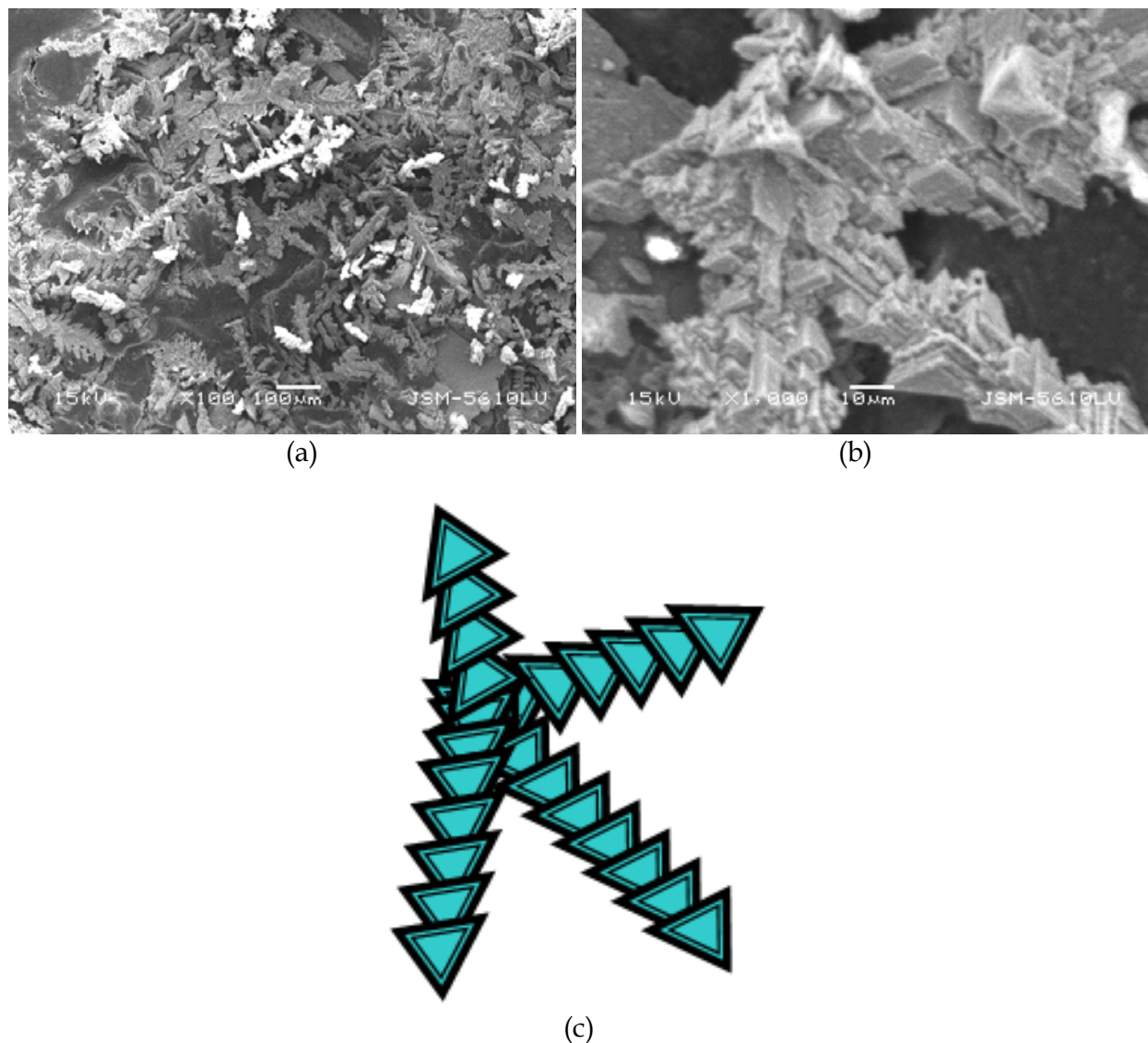


Fig. 14. SEM images of cuprous oxide nanostructures (A) 100 x, (B) 1,000 x, and (C) Schematic illustration of the dendrite structure formation process.

3.5 Metal-polysaccharide nanocomposites

Noble metal nanoparticles dispersed in insulating matrices have attracted the interest of many researchers from both applied and theoretical points of view [34]. The incorporation of metallic nanoparticles into easily processable polymer matrices offers a pathway for better exploitation of their characteristic optical, electronic and catalytic properties. On the other hand, the host polymers can influence the growth and spatial arrangement of the nanoparticles during the in situ synthesis, which makes them convenient templates for the preparation of nanoparticles of different morphologies. Furthermore, by selecting the polymer with certain favorable properties such as biocompatibility [35], conductivity [36] or photoluminescence [37], it is possible to obtain the nanocomposite materials for various technological purposes.

There are several reports of Ag nanocomposites with conducting polymers like polyaniline [38] and polypyrrole [39]. However, electrical conducting properties of green metal - starch

nanocomposites would be of potential biomedical applications. Lyophilisation or vacuum drying of the aqueous solution of starch capped nanoparticles results in metal-starch nanocomposites with high thermal stability and interesting electrical conductivity. The TG Analysis in Fig. 15 shows that the thermal stability of starch can be improved by incorporation of AgNPs [40] making it suitable for conductivity measurements even at high temperature. As the concentration of silver goes on increasing the thermal stability goes on increasing.

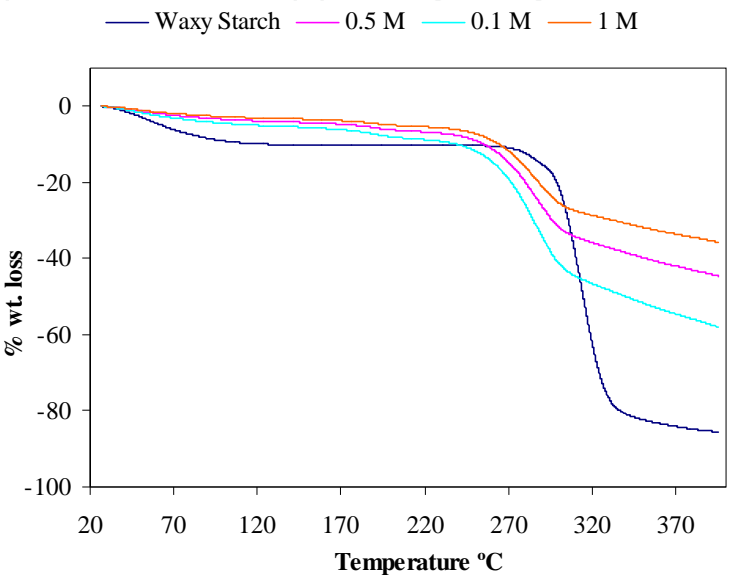


Fig. 15. TGA curve of pure waxy starch and Ag-waxy starch nanocomposites with different concentrations of silver ion precursor (moles of AgNO3)

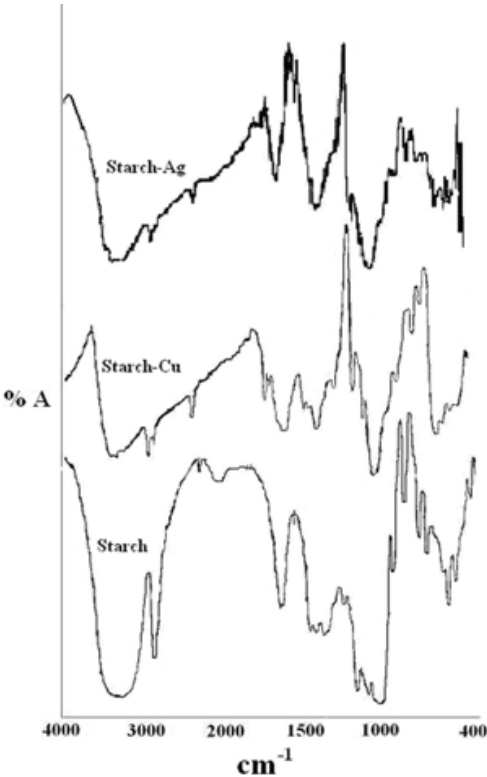


Fig. 16. FT-IR spectra of pure waxy starch and waxy starch metal nanocomposites

The FT-IR spectra of pure of nanocomposites exhibited shift in the absorption frequencies due to the interaction of metal with starch (Fig. 16).

Electrical conductivity measurements revealed that ionic conductivity of Ag-starch nanocomposites increased as a function of temperature (Fig.17) which is an indication of a thermally activated conduction mechanism [40]. This behavior is attributed to increase of charge carrier (Ag^+ ions) energy with rise in temperature. It is also found to increase with increasing concentration of Ag ion precursor (inset of Fig.17). This potentiality can lead to development of novel biosensors for biotechnological applications such as DNA detection.

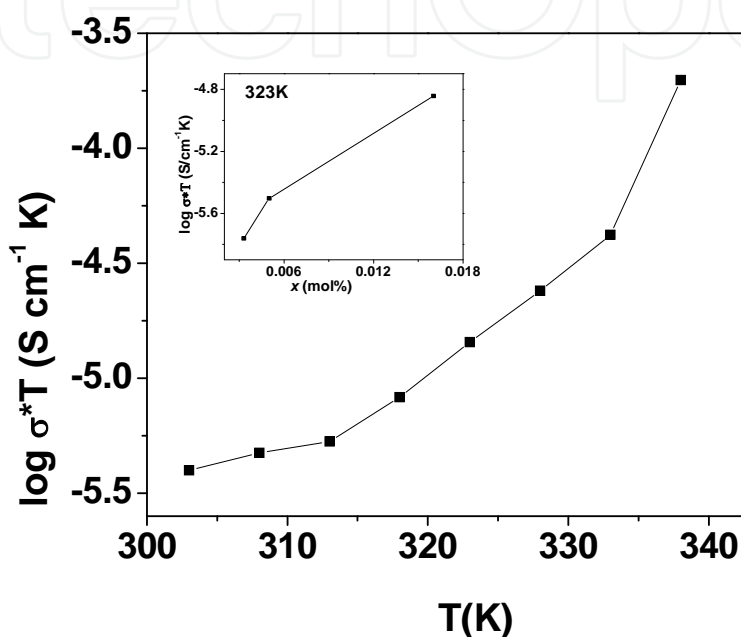


Fig. 17. Variation of conductivity of Ag-starch nanocomposites with temperature. Inset shows variation with concentration of silver nanoparticles.

4. Conclusions

Biopolymers have diverse roles to play in the advancement of green nanotechnology. Nanosized derivatives of polysaccharides like starch and cellulose can be synthesized in bulk and can be used for the development of bionanocomposites. They can be promising substitutes of environment pollutant carbon black for reinforcement of rubbers even at higher loadings (upto 50phr) via commercially viable process. The combined effect of size reduction and organic modification improves filler-matrix adhesion and in turn the performance of polysaccharides. The study opens up a new and green alternative for reinforcement of rubbers.

Starch can also be useful for completely green synthesis of various metallic nanoparticles serving as stabilizing agent as well as reducing agent in aqueous medium. Biopolymer capping offers additional advantages like water solubility, and biocompatibility for biological applications. Water soluble starch capped nanoparticles proved to be efficient non-cytotoxic bactericidal agents at nanomolar concentrations. The investigation also suggested that starch capped CuNPs have great potential for use in biomedical applications such as cellular imaging or photothermal therapy. Biopolymers are also promising biocompatible carrier of

nanoparticles for destruction of tumor/cancer cells. Further attempts to use the biopolymer capped nanoparticles for targeted in vivo delivery to cancer cells are in progress.

Some frequently used Abbreviations

Sr. No	Material	Abbreviations
1.	Waxy corn starch	SW
2.	Cellulose	Cel
3.	Starch nanoparticles	SNPs
4.	Cellulose nanoparticles	CelNPs
5.	Starch acetate nanoparticles	SACNPs
6.	Cellulose acetate nanoparticles	CelAcNPs
7.	Carbon black	CB
8.	Copper nanoparticles	CuNPs
9.	Silver nanoparticles	AgNPs
10.	Starch capped copper nanoparticles	SCuNPs
11.	Uncapped copper nanoparticles	UCuNPs
12.	Parts per hundred parts of rubber	Phr

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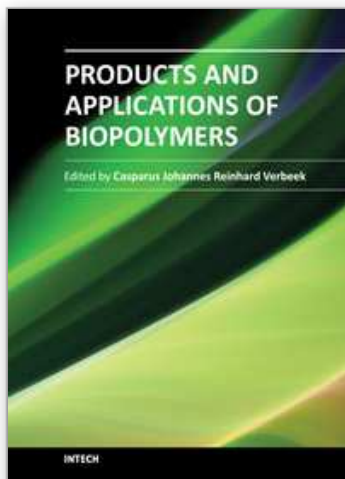
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It is interesting to consider that biopolymers are by no means new to this world. It is only because of our fascination with petrochemical products that these wonderful materials have been neglected for so long. Today we face a different challenge. Environmental pressure is pushing away from synthetic or petro-chemically derived products, while economic factors are pulling back from often more expensive "green" options. This book presents two aspects of biopolymers; potential products and some applications of biopolymers covering the current relevance of biopolymers.

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